



## Short communication

## Performance of a passive direct ethanol fuel cell



J.P. Pereira, D.S. Falcão, V.B. Oliveira\*, A.M.F.R. Pinto\*

Centro de Estudos de Fenómenos de Transporte, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto,  
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

## HIGHLIGHTS

- An experimental study with a passive DEFC with 25 cm<sup>2</sup> of active area is described.
- Tailored MEAs were tested in order to achieve low ethanol crossover rates.
- Thicker membranes and anode diffusion layers lead to low ethanol crossover rates.
- A power density of 1.33 mW cm<sup>-2</sup> was obtained with an ethanol concentration of 2 M.

## ARTICLE INFO

## Article history:

Received 10 July 2013

Received in revised form

20 November 2013

Accepted 9 December 2013

Available online 19 January 2014

## Keywords:

Passive direct ethanol fuel cell

Ethanol crossover

Ethanol concentration

Design parameters

Optimization

Performance

## ABSTRACT

Ethanol emerges as an attractive fuel since it is less toxic and has higher energy density than methanol and can be produced from biomass. Direct ethanol fuel cells (DEFCs) appear as a good choice for producing sustainable energy for portable applications. However, they are still far from attaining acceptable levels of power output, since their performance is affected by the slow electrochemical ethanol oxidation and water and ethanol crossover.

In the present work, an experimental study on the performance of a passive DEFC is described. Tailored MEAs (membrane electrode assembly) with different catalyst loadings, anode diffusion layers and membranes were tested in order to select optimal working conditions at high ethanol concentrations and low ethanol crossover. The performance increased with an increase of membrane and anode diffusion layer thicknesses and anode catalyst loading. A maximum power density of 1.33 mW cm<sup>-2</sup>, was obtained using a Nafion 117 membrane, 4 mg cm<sup>-2</sup> of Pt–Ru and 2 mg cm<sup>-2</sup> of Pt on the anode and cathode catalyst layers, ELAT as anode diffusion layer, carbon cloth as cathode diffusion layer and an ethanol concentration of 2 M. As far as the authors are aware this is the first work reporting an experimental optimization of passive DEFCs.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Fuel cells have been identified as a promising power source for transportation and portable electronic devices, since they convert the chemical energy of a fuel directly into electrical energy, have low emissions and absence of moving parts. The direct fuel cells (DFCs) use liquid fuels as a fuel without a reforming step, have a compact design and potentially can offer up to ten times the energy density of rechargeable batteries. In addition, DFCs can operate at ambient temperature, which significantly reduces thermal management challenges for small systems. These advantages make the technology attractive to the rapid growing need for

portable power sources. However, the DFCs have slow anode kinetics, resulting in higher anodic overpotentials and have fuel crossover through the membrane from the anode to the cathode side, which not only lowers the fuel utilization but also degrades the cathode performance and generates extra heat [1,2]. Among all the investigated possible fuels, liquid alcohol fuels, which have high energy density and are easy to transport, store and handle become an alternative to hydrogen. Up to a few years ago, methanol was the most used fuel and much progress has been made in the development and optimization of direct methanol fuel cells (DMFCs) [3–17]. However methanol is toxic for human beings, is easily volatile and inflammable as well as non-renewable [2–4]. Among the other alcohols available, ethanol appears as an attractive and promising fuel due to its: (i) non-toxicity, (ii) natural availability, (iii) renewability and (iv) higher power density. Based on that, direct ethanol fuel cells (DEFCs) appear as a more attractive technology than DMFCs [1–4].

\* Corresponding authors.

E-mail addresses: [vaniaso@fe.up.pt](mailto:vaniaso@fe.up.pt) (V.B. Oliveira), [apinto@fe.up.pt](mailto:apinto@fe.up.pt) (A.M.F.R. Pinto).

Concerning the different concepts of fuel delivery and handling, the DEFCs can be categorized as passive and active. Active systems need moving parts to feed oxidant and fuel to the cell requiring power to operate. This type of system supply has greater costs and lower system energy density and thus is better suited for large fuel cells. Passive systems use natural capillary forces, diffusion, convection (air breathing) and evaporation to achieve all processes without any additional power consumption. Therefore a passive system is more suitable for portable power sources [5–9]. Like the active ones, the passive systems suffer from ethanol crossover, when the cell is operated with high ethanol concentrations. This leads to a fuel cell performance loss since ethanol diffuses through the membrane generating heat but no power [18–22]. The solution is to use low ethanol concentrations on the anode side. As already mentioned, in passive systems, ethanol is delivered to the catalyst layer by a passive diffusion mechanism, so if ethanol is not supplied adequately and timely, polarization of the cell voltage may occur due to a lack of ethanol. Also, the output of a passive DEFC operating with low ethanol concentrations is not acceptable for real applications. Therefore, low ethanol crossover is essential for using high ethanol concentrations in portable power applications. Different approaches including improving and changing the fuel cell structure have been proposed in the last years for an active feed DEFC [18–26]. However, as the authors are aware, no work on passive DEFC systems was performed.

In DEFCs, water is produced at the cathode, and to avoid some ethanol crossover problems, more dilute solutions are fed to the anode side. This leads to a higher water concentration gradient between the anode and the cathode side, so more water crosses the membrane towards the cathode side due to electro-osmotic drag and diffusion. However, the presence of a large amount of water on the cathode due to the oxygen reduction reaction along with water that permeates from the anode, tends to flood the cathode leading to an increase in oxygen transport resistance and reducing the cell performance [27]. Thus, another important issue on DEFCs is how to remove water from the cathode to avoid several flooding and subsequently supply water to the anode to make up water loss due to crossover through the membrane. Although, some efforts have been made for studying water transport in DMFCs [12–17], a general understanding of water crossover in DEFCs, especially for passive feed systems, is far less understood.

As explained before, the great challenge in passive DEFC systems is how to reduce both ethanol and water crossover without sacrifice of performance. Based on previous work performed with DMFCs, the solution is to use high concentrations of ethanol solutions and use different membrane, diffusion layers and catalyst layers materials with different thicknesses [12–17].

Despite the importance of passive feed systems, until now, no work on optimization of passive DEFC has been reported. Based on that, in this study, the effect of ethanol concentration and the effect of design parameters, such as membrane thickness, anode diffusion layer material and catalyst loading on the cell performance of a passive DEFC was investigated. The cell performance was evaluated and analysed by measuring the current–voltage characteristics at ambient conditions (atmospheric pressure and ambient temperature). The experiments were performed with an «in-house» developed DEFC with 25 cm<sup>2</sup> of active area.

## 2. Experiments

The experimental fuel cell consists of two, 1 cm thick, acrylic end plates (one open on cathode side, and one with a reservoir of 12.5 cm<sup>3</sup> on the anode side), two isolating rubber plates, two stainless steel connector plates (with 36 holes with a diameter of

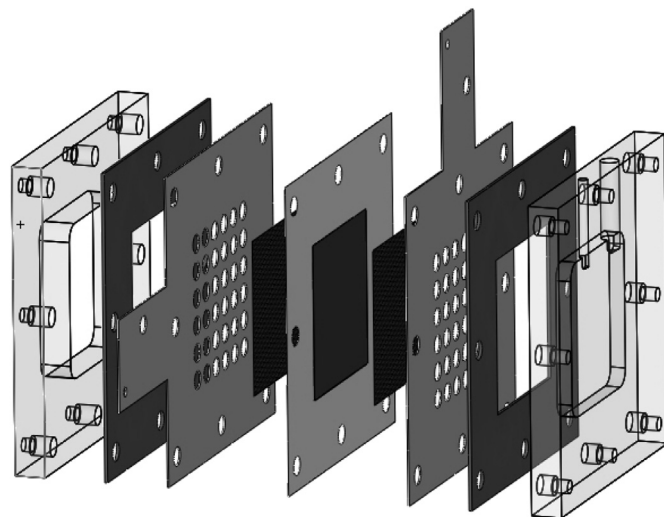


Fig. 1. «In-house» passive direct ethanol fuel cell.

0.6 cm), two diffusion layers, two catalyst layers and a membrane (Fig. 1).

In the experiments, a DEFC with a membrane active area of 25 cm<sup>2</sup> was used and was operated at atmospheric pressure by feeding aqueous ethanol solution to the anode. The fuel cell temperature was controlled by a digital temperature controller and was set near ambient conditions, 20 °C. Three different ethanol concentrations (1–3 M) were tested in order to analyse the effect of the ethanol feed concentration on fuel cell performance. To evaluate the effect of the membrane thickness on the cell voltage and power density two different membranes with different thicknesses were used, Nafion 117 and 115. The catalyst used on the anode and cathode side was, respectively, Pt–Ru black (with a molar ratio of 1:1) and Pt black 60 wt.% on advanced carbon support. Two different loadings were used on the anode side, 4 mg cm<sup>−2</sup> and 2 mg cm<sup>−2</sup> and a loading of 2 mg cm<sup>−2</sup> of Pt was used on the cathode side. The three-layer membranes were supplied by QuinTech. Carbon cloth (CC) (E-TEK, type A), with 30 wt.% PTFE wet-proof treatment was used as cathode gas diffusion layer and three different materials were used on the anode side, carbon cloth (E-TEK, type A, 30 wt.% PTFE), carbon paper (CP) (Toray™ TP-060T, 20 wt.% PTFE) and single-side Pt-catalysed ELAT (E-TEK), which uses carbon cloth as the backing layer. Some structural properties of these materials are presented in Table 1. In order to introduce, as soon as possible, the DEFCs in the market, in this work, we chose to use materials, for the diffusion and catalyst layers and for the membrane, that are commercially available.

The experimental tests were performed with a commercial electrochemical impedance test station (Zahner–Elektrik GmbH & Co. KG) and the polarization curves were performed galvanostatically. The computer constantly monitors both current and voltage and these parameters are used to estimate and track the cell power.

Table 1  
Structural characteristics of the common materials used as gas diffusion layers [15].

Material	Porosity	Tortuosity	Thickness (cm)
CC (Type A)	0.83	1.11	0.035
CP (TP-060T)	0.78	2.75	0.019
ELAT	0.80	1.50	0.040

### 3. Results and discussion

In passive DEFC systems the temperature rises with time due to the electrochemical reactions. Based on that, in order to minimize this effect on the results presented in this section, all the experiments were conducted at a controlled temperature, ensuring a constant temperature value during each test.

Despite the work performed regarding the effect of different operating and design parameters on passive DMFCs, the results and conclusions presented for that type of fuel cell may be not necessary the same for DEFCs, since these two types of fuel cells have different fuels, having for that reason different heat and mass transport properties. They, also, have different reactions on the anode and cathode side, which will contribute for different mass and heat transport phenomena. Therefore, it is very important to evaluate the same effects on passive DEFCs, and the present work accomplish that. It is expected that the performances and power outputs presented in the present section are lower than the ones obtained with a DMFC [7–17], mainly due to the slow ethanol oxidation reaction on the anode side. However, since ethanol is less toxic and can be produced from renewable sources is a more attractive fuel to produce energy for portable applications and work on optimization passive DEFC systems is needed.

The performance of the passive DEFC was determined by a set of tests, in order to obtain the cell polarization and power density curves. The influence of ethanol concentration, membrane thickness, anode diffusion layer material and anode catalyst loading was carefully investigated.

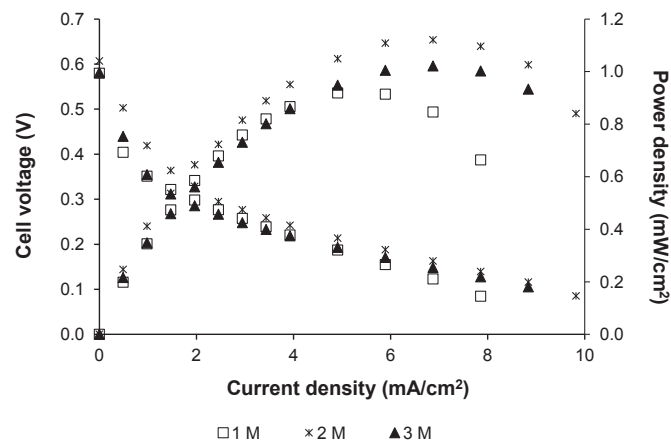
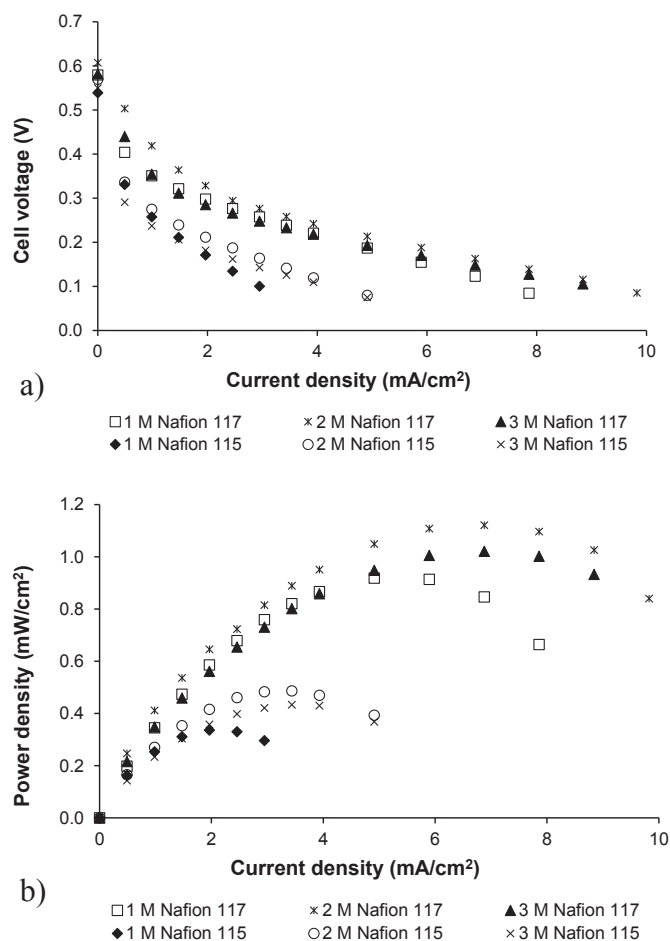
In Fig. 2 the polarization and power density curves for the three ethanol concentrations (1–3 M) tested are presented. A Nafion 117 membrane, an anode catalyst loading of  $4 \text{ mg cm}^{-2}$  Pt–Ru and a cathode catalyst loading of  $2 \text{ mg cm}^{-2}$  Pt was used. Carbon cloth was used as anode and cathode diffusion layers.

The effect of ethanol concentration on fuel cell performance usually have two different effects: a positive and a negative one. An increase on ethanol concentration will lead to an increase on the coverage of the electrocatalyst, increasing the ethanol oxidation reaction, and to an increase of the limiting current density. However, will also lead to an increase of the ethanol concentration gradient between the anode and the cathode side with a consequent increase of ethanol crossover through the membrane. The ethanol that crosses the membrane reacts at the cathode side decreasing the catalytic sites available for oxygen reduction reaction and forming a mixed potential at the cathode side. This will

lead to a decrease of the fuel cell performance and a decrease of the energy density of the system.

It should, also be mentioned that the ethanol concentration is directly related to the water concentration, since more dilute solutions have a higher water content. Higher water concentrations on the anode side will lead to higher water concentration gradients between the anode and the cathode with a consequent increase on the water crossover through the membrane. Also, the water on the anode side will produce no power. Thus, low ethanol concentrations, will have low ethanol crossover rates but higher water crossover rates. Large amounts of water on the cathode side, due to crossover and to water production on the cathode reaction may flood the cathode and decrease the fuel cell performance. Therefore, the effect of ethanol concentration on the DEFC performance is a result of both positive effects on the ethanol oxidation kinetics and limiting current density and the negative ones on ethanol and water crossover.

As can be seen, in Fig. 2, the open-circuit voltage is much lower than the thermodynamic equilibrium cell voltage (1.14 V) mainly due to ethanol crossover. The results also show that the fuel cell voltage and power density increases with an increase of the ethanol feed concentration, until a concentration of 3 M. After this value the negative effect of higher concentrations on ethanol and water crossover seems to be more relevant than the positive ones. When comparing an ethanol concentration of 1 M and 3 M, it can be seen, that for lower current densities, higher concentrations lead to



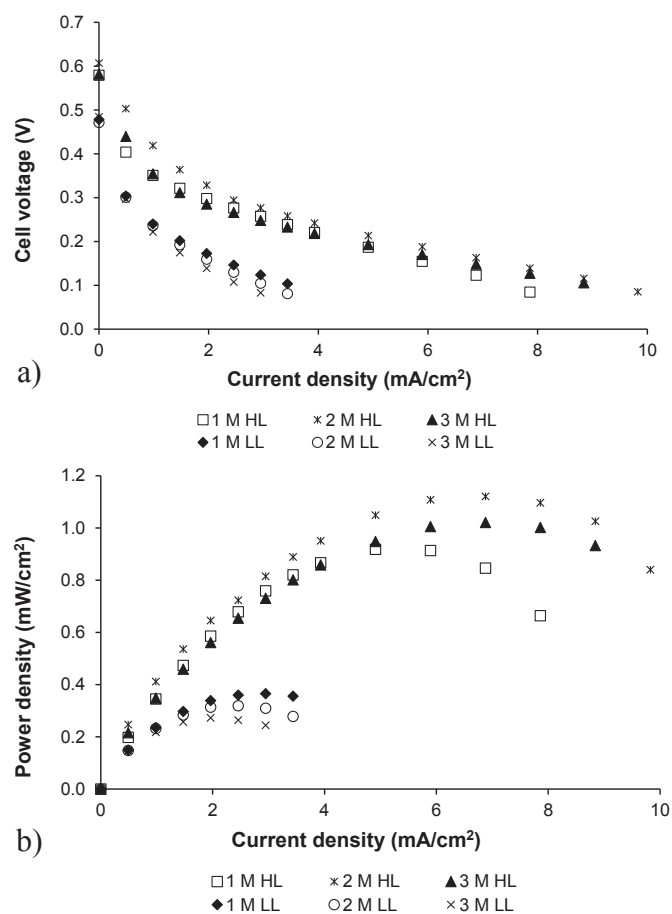
**Fig. 2.** Influence of ethanol concentration on cell voltage and power density. Design parameters: Nafion 117, anode catalyst loading  $4 \text{ mg cm}^{-2}$  Pt–Ru, cathode catalyst loading  $2 \text{ mg cm}^{-2}$  Pt, carbon cloth as anode and cathode diffusion layer.

**Fig. 3.** Influence of membrane thickness on a) fuel cell voltage and b) power density. Design parameters: anode catalyst loading  $4 \text{ mg cm}^{-2}$  Pt–Ru, cathode catalyst loading  $2 \text{ mg cm}^{-2}$  Pt, carbon cloth as anode and cathode diffusion layer.

lower performances, but for higher current densities more concentrated ethanol solutions show a better performance. As explained, higher concentrations have higher limiting current densities due to an increase in the mass transfer rate of ethanol from the anode reservoir to the anode catalyst layer, reducing the anode voltage loss due to mass transfer polarization which is the major loss for high current densities.

To investigate the effect of the membrane thickness on the DEFC performance, a Nafion 117 membrane (thickness 0.18 mm) and a Nafion 115 membrane (thickness 0.127 mm) were used. Fig. 3(a and b) shows, respectively, the effect of membrane thickness on cell voltage and on power density. As can be seen, for the three ethanol concentrations tested (1–3 M), the Nafion 115 membrane had a lower performance than Nafion 117. Although, thinner membranes have low ohmic resistances, they have higher water and ethanol crossover rates. So the effect of membrane thickness on performance is a combined effect of both positive and negative effects. For this specific cell design and for the Nafion 115 membrane, it seems that the negative effect on ethanol and water crossover is more relevant than the positive one on ohmic resistance.

To study the effect of the anode catalyst layer on fuel cell performance an anode catalyst loading (Pt–Ru) of  $2 \text{ mg cm}^{-2}$  (LL – lower loading) and  $4 \text{ mg cm}^{-2}$  (HL – higher loading) was used, and the cathode catalyst loading was fixed at  $2 \text{ mg cm}^{-2}$  Pt. The experimental results regarding the effect of the anode catalyst loading on cell voltage and power density are presented in Fig. 4.



**Fig. 4.** Influence of anode catalyst loading on a) fuel cell voltage and b) power density. Design parameters: Nafion 117, cathode catalyst loading  $2 \text{ mg cm}^{-2}$  Pt, carbon cloth as anode and cathode diffusion layer.

It should be empathized that there are three essential properties of the electrodes that may be affected by variations on the catalyst loading: the active catalyst surface area, the electronic conductivity and the thickness of the electrode. The reduction of the catalyst loading conducts to a reduction of the catalyst layer leading to a reduction of the active surface area, an increase on resistivity with a consequent decrease of ionic conductivity and a decrease of thickness. Therefore, an increase on the catalyst loading leads to an increase on the catalyst active area, so, more active sites are available for ethanol oxidation. This leads to a decrease of the anode overpotential and consequently an increase on fuel cell performance since more ethanol is oxidized on the anode side and less ethanol passes through the membrane to the cathode side. Also, an increase on the catalyst loading causes an increase on electrode thickness. Thicker electrodes have higher mass transport resistances, controlling the rate of ethanol and water reaching the membrane and avoiding in some extent the amount of ethanol and water that crosses the membrane. This reduces the parasite current formed due to the ethanol oxidation at the cathode side increasing the fuel cell performance, and also, the amount of water in the cathode side, avoiding the cathode flooding. Thicker catalyst layers have more ethanol involved in the anodic reaction. However, thicker catalyst layers have higher internal cell resistances with a consequent increase of the ohmic losses. The results presented in Fig. 4, show that a reduction of the noble metal loading leads to a decrease in cell performance, due to an increase on ethanol and water crossover rates and a decrease of the catalyst active area for ethanol oxidation reaction.

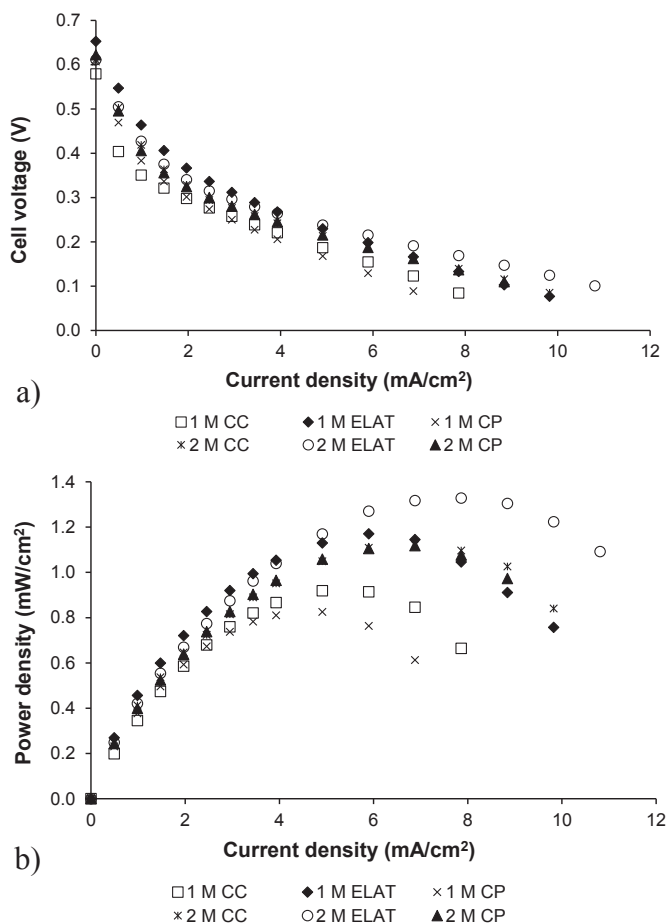
As known, there are three types of materials commonly used as anode and cathode diffusion layers in fuel cells, all of them fiber-based porous materials: carbon cloth, carbon paper and ELAT. These layers are extremely important in a fuel cell since they have a crucial role on the transport and distribution of the reactants, products removal, electrical connection and MEA mechanical support. Different diffusion layers materials have different properties, such as thickness, porosity, tortuosity, wettability and roughness, which will affect the fuel cell performance. As can be seen, in Table 1, carbon cloth is more porous, less tortuous and thicker than carbon paper. ELAT is less porous, thicker and more tortuous than carbon cloth.

In order to evaluate the effect of the anode diffusion layer material on fuel cell voltage and power density three different materials were used, carbon cloth (CC), carbon paper (CP) and ELAT. The diffusion layer on the cathode side was carbon cloth.

Fig. 5 shows the effect of anode diffusion layer material on cell voltage and power density for the three materials tested. The plots from this figure indicate that better performances are achieved using ELAT as anode diffusion layer, mostly due to its treatment with Pt. As mentioned, ELAT has a platinum treatment on one side, the side that is in contact with the catalyst layer, having for this reason an extra catalyst loading. In such conditions, more active sites are available for ethanol oxidation reaction, with a consequent decrease on the anode overpotential and an increase on fuel cell performance.

Regarding the thicknesses of the diffusion layers, it is expected that thicker diffusion layers have higher mass transport resistances, reducing the amount of water and ethanol that reaches the membrane. Therefore, they will have low ethanol and water crossover rates due to a decrease of ethanol and water concentration on the anode catalyst layer. However, lower ethanol concentrations on the catalyst layer surface increase the anode activation overpotentials and decrease the fuel cell performance. This can be seen in the results presented in Fig. 5 regarding the CC and the CP, since for low current densities where the major loss is the activation loss, the CP which has a higher ethanol concentration on the catalyst layer





**Fig. 5.** Influence of anode diffusion layer on a) fuel cell voltage and b) power density. Design parameters: Nafion 117, anode catalyst loading  $4 \text{ mg cm}^{-2}$  Pt–Ru, cathode catalyst loading  $2 \text{ mg cm}^{-2}$  Pt, carbon cloth as cathode diffusion layer.

surface, due to its lower thickness, has better performances. As can be seen in Table 1, CP is less porous than CC, and an increase on porosity increases the ethanol and water concentration on the anode catalyst layer which leads to higher concentration gradients between the anode and cathode side and an increase on the ethanol and water crossover rates. Since the CP is less porous, have low ethanol and water crossover rates, which it is very advantageous especially for low current densities. For high current densities the higher thicknesses of the diffusion layers (CC and ELAT) are advantageous to reduce the amount of ethanol and water that crosses the membrane, avoiding in some extent the water flooding problems and the formation of the mixed potential on the cathode side. This leads to better fuel cell performances.

It should also be mentioned that, on the anode side, gaseous carbon dioxide is produced by the anodic reaction and must be efficiently removed from the catalyst layer. The ability of a material to remove the products from the catalyst surface greatly influences the cell performance, since if the carbon dioxide bubbles cannot be removed from the catalyst surface they cover the surface decreasing the effective active area for ethanol oxidation. This situation occurs mainly for high current densities where the two-phase mechanism are present. The texture or carbon paper with a highly tortuous structure enhances the interactions between the bubbles and the solid (Table 1) and the gas tends to remain attached to the surface leading to a blockage of the active sites, lowering the ethanol oxidation reaction rate and the cell performance. This explains the loss in performance for high current

densities when CP is used as diffusion layer instead the other two materials.

#### 4. Conclusions

Low ethanol crossover is essential to improve the performance of DEFCs and achieve higher power densities. Therefore it is crucial to understand the effect of different design and operating parameters on ethanol crossover.

In this work, the effect of ethanol concentration, membrane thickness, anode diffusion layer material and anode catalyst loading on fuel cell performance was studied.

High ethanol concentrations achieve lower fuel cell performances due to the higher ethanol crossover rates generated, however using lower ethanol concentrations significantly reduces the system energy density since more water is present on the anode side, producing no power and will take up a large volume in the fuel reservoir. For this specific cell design the optimum ethanol concentration is around 2 M.

Increasing the membrane and the anode diffusion layer thickness, as well as, the anode catalyst layer, by increasing the catalyst loading could significantly lower the lost in performance due to ethanol and water crossover.

In this work the maximum power density,  $1.33 \text{ mW cm}^{-2}$ , was obtained using a Nafion 117 membrane,  $4 \text{ mg cm}^{-2}$  of Pt–Ru and  $2 \text{ mg cm}^{-2}$  of Pt, as respectively, anode and cathode catalyst layers, ELAT as anode diffusion layer, carbon cloth as cathode diffusion layer and an ethanol concentration of 2 M.

The results presented with a passive feed DEFC showed that changes in the structure of the different fuel cell components are an effective way of controlling the ethanol and water crossover and increasing the fuel cell performance.

#### 5. Further work

The present work is a starting point for more detailed experimental studies aiming to found tailored MEAs with low ethanol and water crossover rates, suitable for DEFC portable applications. New catalyst will be developed and tested in order to obtain better performances and the power outputs needed for portable applications.

Since mathematical models are a useful tool for understanding the fuel cell internal processes (reactions, mass and heat transport) which cannot be observed directly in experiments, a mathematical model considering the effects of coupled heat and mass transfer, along with the electrochemical reactions will be developed.

#### Acknowledgements

V.B. Oliveira acknowledges the post-doctoral fellowship (SFRH/BDP/91993/2012) supported by the Portuguese “Fundação para a Ciência e Tecnologia” (FCT), POPH/QREN and European Social Fund (ESF). POCI (FEDER) also supported this work via CEFT.

#### References

- [1] W.J. Zhou, B. Zhou, W.Z. Li, Z.H. Zhou, S.Q. Song, G.Q. Sun, Q. Xin, S. Douvartzides, M. Goula, P. Tsiakaras, *J. Power Sources* 126 (2004) 16–22.
- [2] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.M. Léger, *J. Power Sources* 105 (2002) 283–296.
- [3] K. Sundmacher, *Ind. Eng. Chem. Res.* 49 (2010) 10159–10182.
- [4] U.B. Demirci, *J. Power Sources* 169 (2007) 239–246.
- [5] S.K. Kamarudin, F. Achmad, W.R.W. Daud, *Int. J. Hydrogen Energy* 34 (2009) 6902–6916.
- [6] F. Achmad, S.K. Kamarudin, W.R.W. Daud, E.H. Majlan, *Appl. Energy* 88 (2011) 1681–1689.
- [7] X. Li, A. Faghri, *J. Power Sources* 226 (2013) 223–240.

- [8] A. Faghri, Z. Guo, *Appl. Therm. Eng.* 28 (2008) 1614–1622.
- [9] T. Shimizu, T. Momma, M. Mohamedi, T. Osaka, S. Sarangapani, *J. Power Sources* 137 (2004) 277–283.
- [10] Y. Zhu, J. Liang, C. Liu, T. Ma, L. Wang, *J. Power Sources* 193 (2009) 649–655.
- [11] C.E. Shaffer, C.Y. Wang, *J. Power Sources* 195 (2010) 4185–4195.
- [12] C. Xu, A. Faghri, X. Li, T. Ward, *Int. J. Hydrogen Energy* 35 (2010) 1769–1777.
- [13] C. Xu, A. Faghri, X. Li, *Int. J. Hydrogen Energy* 36 (2011) 8468–8477.
- [14] X. Li, A. Faghri, C. Xu, *Int. J. Hydrogen Energy* 35 (2010) 8690–8698.
- [15] V.B. Oliveira, C.M. Rangel, A.M.F.R. Pinto, *Int. J. Hydrogen Energy* 34 (2009) 6443–6451.
- [16] V.B. Oliveira, C.M. Rangel, A.M.F.R. Pinto, *Int. J. Hydrogen Energy* 34 (2009) 8245–8256.
- [17] V.B. Oliveira, D.S. Falcão, C.M. Rangel, A.M.F.R. Pinto, *Int. J. Energy Res.* 37 (2013) 991–1001.
- [18] S. Heysiattalab, M. Shakeri, M. Safari, M.M. Keikha, *J. Ind. Eng. Chem.* 17 (2011) 727–729.
- [19] S. Song, P. Tsiakaras, *Appl. Catal. B Environ.* 63 (2006) 187–193.
- [20] G. Andreadis, P. Tsiakaras, *Chem. Eng. Sci.* 61 (2006) 7497–7508.
- [21] G. Andreadis, A.K.M. Podias, P. Tsiakaras, *J. Power Sources* 181 (2008) 214–227.
- [22] Y.H. Chu, Y.G. Shul, *Fuel Cells* 12 (2012) 109–115.
- [23] H. Pramanik, A.A. Wragg, S. Basu, *J. Appl. Electrochem.* 38 (2008) 1321–1328.
- [24] Q. Wang, G.Q. Sun, L. Cao, L.H. Jiang, G.X. Wang, S.L. Wang, S.H. Yang, Q. Xin, *J. Power Sources* 177 (2008) 142–147.
- [25] I. Kim, O.H. Han, S.A. Chae, P. Younkee, S.H. Kwon, K.S. Lee, Y.E. Sung, H. Kim, *Angew. Chem. Int. Ed.* 50 (2011) 2270–2274.
- [26] V. Alzate, K. Fatih, H. Wang, *J. Power Sources* 196 (2011) 10625–10631.
- [27] K. Jiao, X. Li, *Prog. Energy Combust.* 37 (2011) 221–291.